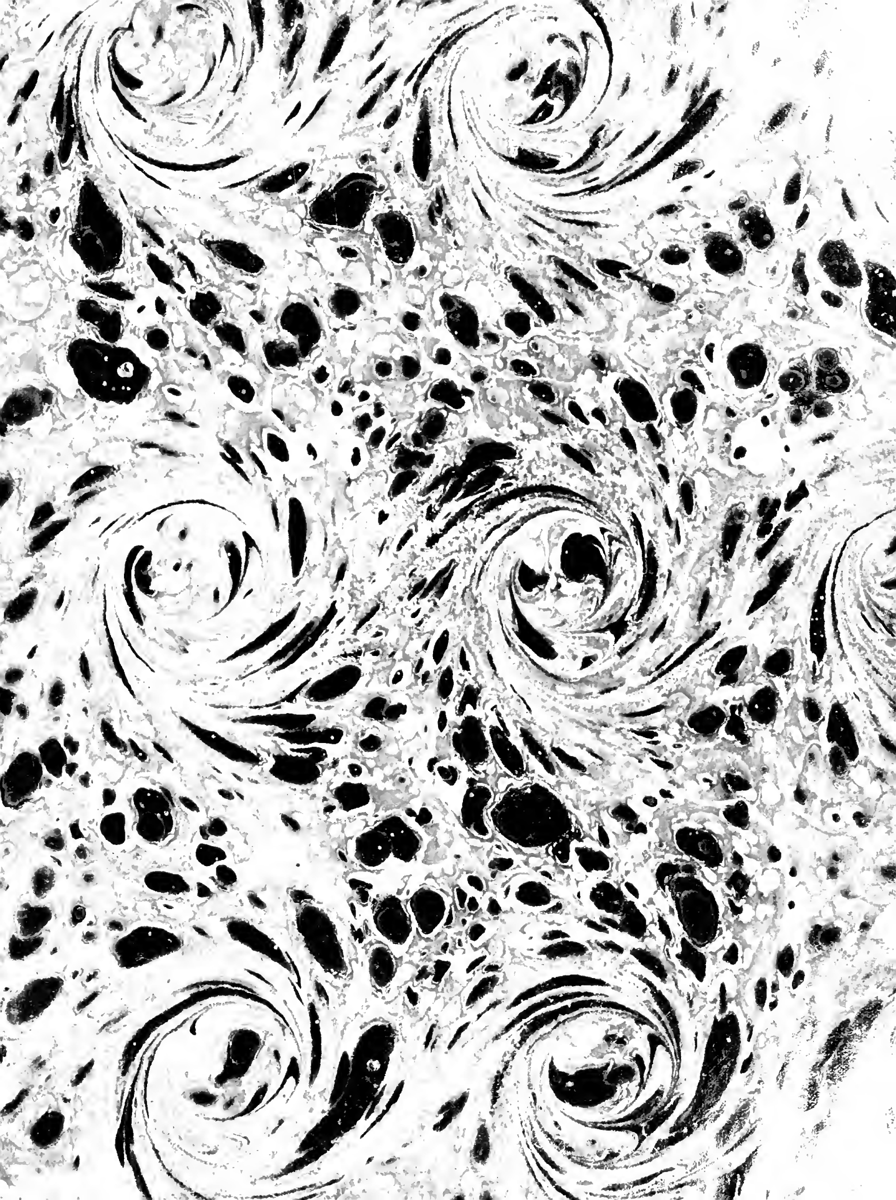

THE JOULE-THOMSON EFFECT FOR AIR
AT MODERATE TEMPERATURES AND PRESSURES.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES

OF THE JOHNS HOPKINS UNIVERSITY

IN CONFORMITY WITH THE REQUIREMENTS FOR THE

DEGREE OF DOCTOR OF PHILOSOPHY.

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BALTIMORE

1916.

172,387

CONTENTS.

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Introductory.

Historical Outline:- Since the original experiments of Joule and Thomson[1], which were carried out in the years 1852 to 1862 there has been felt, on the part of physicists, that owing to their great scientific and technical importance, their results should be repeated, extended and refined with use of modern methods of measurement and with greater precaution as to details. The gases with which they worked were air, nitrogen, oxygen, carbon dioxide and hydrogen.

Later Regnault[2] took up the problem for a while, finally abandoning it with an expression of regret for the time he had wasted upon a research 'so sterile'. For he found he could attach no meaning to the measurements of temperature on the low-pressure side of the plug, so erratic were the results obtained.

Again, Hirn[3] worked on steam. A number of others, such as Griessmann[4], Grindley[5], Peake[6] and Dodge[7] performed throttling experiments on steam, the first using a porous plug very much like that of Joule and Thomson while the other three used what engineers call a throttling or "wire-drawing calorimeter".[8] Their purpose was to determine the variation of the specific heat of superheated steam with pressure and temperature, which has been better done in other ways.

Cazin[9] in 1870 published an account of experiments which were actually modifications of the Gay-Lussac free-expansion experiment. His apparatus was complicated and, he admits, his results were qualitative.

Natanson[10] in 1887 described porous plug experiments on carbon dioxide at 20°C only. His pressure-drop was about one atmosphere and his highest absolute pressure 25 atm.; and between the lowest and highest pressure he found a decided dependence of the cooling effect upon pressure, whereas Joule and Thomson had been unable to detect (up to 6 atm.) any such effect. This dependence does not agree with that found later by Kester and is in the opposite sense from that found for air in the present paper. The latter is hardly to be expected even though the gases are different.

Kester[11] extended the work of Natanson to temperatures between 0° and 100° finding also a dependence upon pressure. The results of the two observers are not in agreement, Kester's results at the same temperature (20° C) being independent of pressure up to the highest pressure, 41 atm., that was available, while the work of Natanson yielded a positive pressure coefficient.

Olszewski[12] performed experiments, using not a porous plug but a throttle valve, on hydrogen with a view to determining its "inversion temperature" as bearing upon the problem of its liquefaction. The

high pressure of the experiment varied from 117 to 170 atm. and the low pressure was uniformly one atmosphere. The one datum of this experiment was -80.°5 for the inversion temperature under these conditions. The effect observed here was, of course, an integrated one and leaves much to be desired for application of thermodynamic equations.

Five years later[13] (1907) he did the same thing for nitrogen and air, finding a series of inversion points for magnitudes of the pressure-drop varying from 160 atm. to 30 atm.

Rudge[14] carried out (1909) a few experiments on carbon dioxide supplied on the market in the form of "sparklets" for making carbonated water. The duration of each experiment was but a few minutes and the author does not attach great importance to the results but offers them in view of the scanty known data. It would seem that the ideal conditions for continuous-flow methods could hardly be realized in so short a time.

Bradley and Hale[15] in the same year carried out experiments upon "the nozzle expansion of air at high pressure", i.e. from initial pressures of 70 to 200 atm. to final pressures of 1 atm. Their temperatures extended from 0° C to -120° C approximately.

Their apparatus was a liquefier of the Hampson type and the air expanded, not through a porous plug but a specially constructed

"nozzle". Their special problem was the process of liquefaction; and their results were only in qualitative agreement with those of Joule and Thomson.

Again in the same year (1909) Dalton[16] carried out similar nozzle experiments in air at 0^{o} C only and for pressure drops from about 5 to 40 atm. His results agree with the Joule and Thomson figures at 0^{o} and he notices no pressure effect although his curve would indicate an extremely slight one.

Vogel[17], whose original paper I have not been able to consult, carried out porous plug experiments in the Laboratory of Technical Physics of the Techniche Hochschule in Munich. He was looking for and found a pressure effect while the temperature of his experiments was limited to 10^{o} C.

Noell[18], whose original paper likewise I have been unable to secure, but an abstract of which[18] I have read, continued the work of Vogel using the same apparatus. His pressure-drops were 6 and 8 atmospheres while the arithmetic mean of the absolute high-side and low-side pressures varied from 25 to 150 atm. His high-side temperatures varied from -55^{o}C to $+250^{o}$C. He worked with air only. He found a pressure as well as a temperature effect which he embodied in the interpolation formula:—

$$\frac{\Delta T}{\Delta p} = \frac{50.1 + 0.0297\,p}{T} + \frac{14830 - 1.674\,p}{T^2} + \frac{366000 - 19093\,p}{T^3} - (0.122 + 0.0000157\,p)$$

evidently an empirical expansion in descneding powers of T whose coefficients are linear functions of p.

The units seem to be kg. per cm. in the left-hand member and atmospheres on the right. The difference would not be more than about 3% but the author does not make it clear. The deviations of his observed values from those calculated by this formula vary from 2% to 6% at the lower temperatures to 50% and over at the highest temperatures. Nevertheless it seems to be more systematic and satisfactory than the work of his predecessors, certainly for air.

Mention is made here of work reported by Witkowski[19], who carried out experiments on air at high pressures which passed through a succession of porous plugs. His paper has not been available but only a brief abstract, which contains no quantitative results. I cannot see any theoretical advantage to be gained by a succession of plugs. All the data could be had from a single plug by properly choosing pressures.

Buckingham[31] has proposed a modified form of the porous plug experiment in which the process is rendered isothermal by supplying heat, say electrically, to the plug just sufficient to neutralize the

temperature-drop . If there should be a heating effect, as with hydrogen, then heat would have to be abstracted in some way. No one has ever published work on this method.

It is perhaps out of place to mention it here, but Roebuck[20] has even carried out a porous plug experiment on liquid water near 4° C in order to determine the mechanical equivalent of heat. His results he regards as lacking in accuracy.

The review of the work of these experimenters reveals first a lack of meaning to be attached to their results. For the Joule-Thomson effect enters into the thermodynamic equations as the limiting value of a ratio; the ratio of the temperature-drop to the pressure-drop as these each approach zero. The pressure-drops of Joule and Kelvin were up to 5 or 6 atmospheres, those of Noell 6, 8 and 10 atmospheres, the others still more. Natanson and Kester, however, limited their drops to 1 atmosphere which seemed satisfactory, but that was in carbon dioxide only. About all the work that has so far been found available for the calculations of the thermodynamic scale[21,22,23,23] has been that of Joule and Thomson principally, the later calculations including the results of Natanson and Kester and, in one instance, that of Olszewski.

A second point that impresses one is the omission of any systematic experimental study of sources of error. One short cut seems to

have been in resorting to high pressures, high pressure-drops and a large quantity of gas. For expensive gases the latter procedure would constitute a serious objection.

Further it has seemed on the whole that the experimenters were, perhaps, too ambitious in the direction of extreme temperatures and pressures and not careful enough of sources of error; that perhaps there were too many problems in technique to be attended to at one time.

The need, too, for more accurate data on the Joule-Thomson effect is being felt and occasionally expressed by physicists. Thus Ross-Innes[23] says in part: "The most simple and at the same time the most effective method of meeting the difficulty (i.e. of attaining the thermodynamic scale of temperature) would be to repeat the Joule-Thomson experiments .....".

From considerations such as the above, therefore, and from the results of a year's preliminary experiments in the physical laboratory of the Johns Hopkins University, the present author decided to postpone experimental problems of extreme temperatures and pressures and first attack directly the development of a method. This accomplished, the other would follow. With such an apparatus, moreover, an investigation over any convenient temperature and pressure range would be worth-while —

the main difficulty being to obtain reproducible results.

General Conditions of Present Experiment:- The range of temperatures was confined approximately to the fundamental interval-actually from 15°C to 90°C although experiments had been started at 110° C when the apparatus called for repair. The term "pressure" in the title of this paper refers to the arithmetic mean of the absolute pressures on the two sides of the plug. The range lay from about 6 to 8 1/2 atmospheres, or more precisely, from 4.5 to 6.4 meters of mercury. The pressure-drop ranged from 0.25 to 0.80 meters of mercury. Pressures throughout this paper will be expressed in meters of mercury. For the immediate purpose of these experiments outlined above, the natural gas to be chosen was, of course, air.

Remarks on Theory.

The general theory of the plug experiment has been given so often in treatises and in journal articles that a full treatment of it here would be out of place. As much, however, should be given as is sufficient to define the necessary symbols and to develop such special formulae as are needed in the computation of results. In addition I would bring out a certain point as to the definition of the Joule-Thomson coefficient that I think has not received the emphasis

it deserves. This will involve a brief outline of the general theory first.

On applying the first law of thermodynamics to the process of the porous plug experiment and noting that there is no gain or loss of heat from without and that the rigid plug does zero work on the gas, and that the total work done on each gram of the gas before and behind the plug is $p_1 v_1 - p_2 v_2$, the relation

$$u_1 + p_1 v_1 = u_2 + p_2 v_2$$

holds where the subscripts are conventional and u stands for the intrinsic energy per gram, and where the kinetic energy of stream-line motion may be neglected.

Now the function $u + pv$, the so-called "<u>enthalpy</u>" of Kamerlingh Onnes or Gibbs' heat function, is the same in the regions of equilibrium above and below the plug. Let us call it H. Then we may <u>define</u> the Joule-Thomson coefficient (μ) which is the limiting value of the ratio of the temperature-drop to the pressure-drop, when these each approach zero, under the condition H = const., by the relation

$$\mu \equiv \left(\frac{\partial T}{\partial p}\right)_H \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

From this quickly follows the usual relation (2) when we apply the second law of thermodynamics, as follows:

Calling s the entropy

$$Tds = du + pdv = dH - vdp$$

or, putting T = constant

$$T\left(\frac{\partial s}{\partial p}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T - v$$

But $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$ .... ("thermodynamic relation")

and $\left(\frac{\partial H}{\partial p}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_H = -c_p \mu$

$$T\left(\frac{\partial v}{\partial T}\right)_p = v + \mu c_p \quad \text{.................................} \quad (2)$$

After arriving at this form of treatment I found that a very similar one had been given by Callendar[22].

A great advantage to my mind to be gained in the point of view of the definition (1) is, that if we plot on a t - p diagram, starting from fixed initial conditions, a succession of points corresponding to a succession of pressure and temperature drops, we shall obtain a curve of constant H the slope of whose tangent at any point, therefore, is the value of the Joule-Thomson coefficient at that point. The absolute pressure and temperature for this point would be equal to the initial pressures and temperatures minus the respective pressure and temperature drops to the point in question on the diagram. If this slope in any given case be derived from the chord between two points,

then the proper absolute pressures and temperatures would correspond as a first approximation, to the middle point of the chord. This point will be made use of later in discussing results.

A second advantage in this point of view is in enabling one to draw a contrast with the true free expansion or Gay-Lussac effect, which,, expressed in the same coordinates, is

$$\left(\frac{\partial T}{\partial p} \right)_u$$

a distinction worth noting.

An important experimental consequence, moreover, is that the observer need not determine his temperature readings that correspond to a zero pressure drop, since, as will be noted later, the difference between the mean temperature and the high-side temperature (bath temperature) is negligible in expressing μ as a function of temperature.

It will be shown later that μ is found to be a function of temperature and pressure. In the search for an empirical formula to express this relation and one which would have a little more rational basis than a mere power series, resort was had to the equation of Van der Waals. While this equation does not strictly fit the measurements on isotherms, yet I am in accord with Berthelot[25] in thinking it a valuable index to the broad features of the properties of gases. Further it is something more than an empirical interpolation formula.

Applying to Van der Waals' equation, namely

$$\left(p + \frac{a}{v^2} \right) (v - b) = R\,T ,$$

the relation (2) above, we get, keeping only terms of the <u>second order</u> in the small quantities a and b, the relation

$$\mu\, c_p = - b + \frac{2a}{RT} - \left(\frac{6ab}{R^2 T^2} - \frac{4a^2}{R^3 T^3} \right) p \quad \ldots\ldots\ldots \quad (3)$$

Now the variation in c_p within the limits of the present investigation is small or at most may be considered a linear function of p. If then we neglect the term in T^3 μ should be a function of the form

$$\mu = A + \frac{B}{T} + p\,\frac{C}{T^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

The first two terms are those of the complete formula of Rose-Innes[23]. It willbe noted that the pressure effect is linear and only comes in if we retain second order terms. Later this formula as well as a five-constant power series linear in p and of the second degree in t^0 C will be fitted to the observations. Obviously the second power in T in (4) could be replaced by the first power and the adjustment be empirically just about as good within the small range of observed temperatures, but the second power is retained to keep closer to the original proposed basis of rationality.

Description of Apparatus.

The Air Circuit:-

The air- circuit and the disposition of the various parts are shown in Fig. I. Air is drawn in by the compressor at the intake A which is kept open all the time in order to replenish the supply of air lost by slow leakage. The air then passed upward through the driers D and D', the former containing a column of about a meter of calcium chloride, the latter about half a meter of soda-lime to remove carbon dioxide followed by a half meter of calcium chloride to remove the water put in by the reaction of the carbon dioxide with the soda-lime. Water trapped in the lower end of D from the air under compression is drawn off by the valve B. This was done usually once during a run which lasted some four or five hours.

From the driers the air is carried through a quarter-inch gas pipe to the plug apparatus proper in a neighboring room. Here it passes first through a series of throttling needle-valves t,t,t, then through a third drying tube D" containing phosphorus pentoxide. From this it passes through copper "automobile tubing" of about 5 mm. outside diameter, into the bath, under the surface of which the automobile tubing continues for about two meters, connecting thence with a coil of larger pipe of brass and about one cm. internal diam-

eter and 6 meters in length. This coil terminates in the plug casing P. After passing through the porous plug, the air leaves the casing by way of another length of automobile tubing much shorter than the first and soldered parallel with it for a purpose stated below.

Interchanger:- For a length I I of about a meter the tubes are soldered together side by side forming this a heat interchanger, so that when the bath and the room were at considerably differing temperatures the air leaving the bath would be brought to approximately room temperature and the air entering the bath would be brought to approximately the bath temperature in advance. This device was found to be necessary for two reasons: first, it conserved the heat of the bath and improved its temperature regulation, and secondly, it prevented the throttles t' in the return line from progressively warming, a condition which was found seriously to interfere with pressure regulation. This warming of the valves would gradually change their opening and hence change the rate of flow of air through them.

After leaving the low pressure throttles t', t', t', t' the air returns to the compressor by way of a receiver R of about 10 litres capacity. Curiously enough this receiver was quite effective in reducing the pulsations in the air-circuit produced by the action of the compressor when placed on the low pressure side of

the compressor, while no receiver was needed at all on the high pressure side. It is quite possible to omit R, however, when it is desired to reduce capacity on account of expensive gases.

Pressure Regulation:- It is obviously very necessary to provide means to keep constant the pressures at all points and especially the pressure-drop in passing through the plug. The heat of compression liberated here might quite mask the Joule-Thomson effect. It was observed, for instance, on one occasion that a fluctuation in the pressure-drop of 0.1 percent resulted in a fluctuation of about 5% in the temperature-drop. Special precautions therefore were necessary to provide good pressure regulation and this had to be automatic in the absence of any assistance to the observer.

Rough pressure regulation was attained as a preliminary by placing an adjustable spring safety-valve S (Fig. I) in a by-pass from the high pressure to the low pressure lines near the compressor. This was usually set so that the difference on the two sides of the valve would be from 80 to 160 lbs., gauge reading, depending upon requirements at the plug.

Superposed upon this was a finer method of regulation which was designed to control the pressure drop between the points E and F

(Fig. I). This was carried out by means of an electrically controlled valve mechanism actuated through contacts in a mercury manometer M' which was connected in at the points E and F. The valve mechanism is indicated at PC which is connected as a by-pass to the first or upper throttle t so that when opened the flow of gas is increased.

The two electrical contact-points of the manometer M' are set at any desired difference of level such that the tops of the mercury columns play just under them when the device is functioning properly. If for some reason the pressure difference decreases, the lower contact will be made, and this will actuate one of the electromagnets at PC, which, by a suitable mechanism to be described below, will open the by-pass valve at PC slightly, thus supplying an increased flow of air and bringing the pressure difference back to its proper value. A similar action in the reverse direction will take place if the pressure drop exceeds the limits set by the positions of the contact points. When the pressure is at its proper value, the valve at PC is at rest.

There were of course small fluctuations in pressure remaining even though this device gave much finer regulation than did the safety-valve S. These residual fluctuations were practically damped out by the throttles t t and t' t' lying between the points E F and the plug. The greatest variations in the pressure drop at the plug were of the order of 0.1 mm of mercury and usually too small

to estimate in the field of the telescope.

The throttles t t t t and t't't't' together with the safety-valve S served, in addition as a means of setting the absolute pressures in the system to any desired values.

The details of the valve mechanism are shown in Fig.2. A and B are the two electromagnets connected to the two contact points in the manometer M' (Fig. I) above mentioned. C is a wheel kept continuously in rotation by a thread belt PP. D and D' are two friction drums mounted on the highest speed axle of a wheel train. The wheel C is mounted in trunnions in such a manner, as is obviously shown, that when the magnet A is energized C is pressed against D, when B is energized C is pressed against D'. This evidently reverses the direction of rotation of the drums D and D'. When neither A nor B are energized, the drums are at rest.

The motion this imparted to the wheel train is reduced in the train and transmitted through the drum U, thread T and lever L to the needle valve V. The thread T is kept taut by the spring S. The train includes all the wheels of a 24-hour dollar clock. The fastest wheel would rotate about 2 or 3 times a second. This great reduction of motion was found to be necessary on account of the extraordinary sensitiveness of the air flow to a slight change in the orifice of the valve.

The magnets were wound with 750 ohms each of No. 40 magnet wire and operated on 30 volts. With 5000 ohms shunted across the manometer contact gaps sparking and contamination of the mercury was effectually prevented.

It may be remarked, in passing, that the valve V (Fig.2) was for a time connected as a by-apss between the points E and F (Fig. I) but the arrangement shown proved superior.

Mounting of thermometers:- T_1 and T_2 (Fig. I) are brass tubes housing the stems of platinum resistance thermometers, one of which is situated in the elbow, O on the high-pressure side of the plug, and the second in the interior of the plug casing P. Emerging from the tops of these tubes and passing through sealed joints in appropriate hard rubber insulation are the leads which connect through heavy lamp-cords to the bridge. Into the latter they are connected differentially as will be described later. Thermometer tube T_2 has a telescoping joint indicated in the diagram whose purpose is to permit one to shift vertically the thermometer coil inside P and thus to explore the region on the low-pressure side of the plug in order to study the distribution of temperature therein.

The Differential Manometer:- From the sides of the stems of the thermometers T_1 and T_2 lead two small tubes connected to the manometer M as shown in Fig. I. The latter is thus put in communication with the spaces occupied by the thermometer coils themselves and is

intended to measure the pressure-drop between the high and low pressure sdies of the plug. To test this, readings were taken with the plug removed and the air flowing at the highest speeds of the later experiments. No sensible pressure difference was noted. The manometer was somewhat over a meter in height and was furnished with a brass meter-bar of the "H" form made by the Société Genevoise. This was placed between the tubes and read by a micrometer telescope from a distance of about one meter, the tube and scale being in the same field of view at one time. The crosshair was leveled by setting on the image of the level surface of mercury placed in a glass cell with plane sides at the same distance from the telescope as was the manometer. The heights of meniscus were read off so as to apply the capillary correction which never exceeded 1 mm., and if omitted, would not have introduced an error exceeding 1/500 of the observed pressure drop, and even that would be within the accuracy demanded, for errors of one percent in the Joule-Thomson effect came in from other sources. The corrections, however, were applied making use of the tables given in Kohlrausch, "Physical Measurements" 3rd edition (English) p. 440. The internal diameters of the tubes varied from 5.0 mm to 5.7 mm. along the portions where readings were made.

The readings were likewise reduced to zero, making use of tables

given in Landolt and Börnstein's "Tabellen", 3d Aufl. pp. 34 and 35. Pressures throughout this paper are expressed in meters of mercury at 0°C and for gravity at the University of Virginia, whose value need not be used except in the final formulae.

Pressure Gauges:- To the high-pressure side of the differential manometer were connected a piston gauge and a dial gauge G and G' (Fig. I) respectively. The latter was used for setting to the desired absolute pressures; while the former yielded their correct measure. The piston was of 3/8" drill rod mounted in a snugly fitting brass cylinder provided with a leather packing at the top, so curved as to become tighter as the pressure increased. This also insured that the effective area of the piston was its own cross section and not a compromise between this and that of the bore of the cylinder. Provision was made for rotating the piston, in a manner similar to that carried out by Amagat and thus eliminating the static friction.

The diameter of the piston measured by two micrometer calipers came to 0.9536 cm. giving an area of 0.7142 sq. cm. Thus 1 kg. on the piston corresponded to a pressure of 1.030 meters of mercury at 0° C and at the same locality.

The weights were adjusted by a set of platinum plated weights furnished by Rueprecht of Vienna, and brought to within 0.02% of accuracy

or about 1/50 of the errors of reading of the gauge when in use. Great accuracy was not needed, for it will be seen that the effect of pressure on the Joule-Thomson coefficient is small.

Bath and Thermostat:- The bath was about 90 cm. deep and 30 cm. in diameter with triple walls of brass. The space between the middle and inner wall was filled with asbestos and that between the middle and outer was designed for the circulation of steam, which later was found needless. The outer wall was lagged with asbestos. The cover was lagged with about 10 cm. thickness of cotton waste which has been all that was necessary for temperatures up to 130° C. "Renown engine oil" made by the Standard Oil Co. was used to fill the bath and, on account of its great thermal expansion, a siphon overflow had to be provided. It asphalts appreciably at the higher temperatures and is therefore open to objection. Rapid circulation was provided by two motor-driven propellers on one vertical shaft rotating in a well. The stirrer and heating coils are not shown in the diagram.

Heating was applied electrically from a 220 volt D.C. circuit, through four coils totaling a capacity of one kilowatt. These could be cut in independently in series or in parallel, various combinations being used including auxiliary resistances, according to the temperature of the bath.

Thermostatic control was obtained by keeping a steady current in

some of the resistances and varying the current in the remainder.

This was done automatically by a type of thermostat whose principle is similar to that of Darwin[26] or of Randall[27] and later made use of by the Leeds and Northrup Co. Two of the four arms of a Wheatstone bridge (of about 100 ohms each) are situated in the bath - one of these is of nickel and the other of an alloy known to trade as "therlo". The former has a high temperature coefficient, the latter practically none. The other two arms of resistance alloy were immersed in a small continuously stirred bath at room temperature. The latter arms being in the form of a helical slide wire, could readily be set to any desired ratio. This bridge would obviously balance at some fixed temperature and not at any other. The thermostatic principle consisted in utilizing the deflections of the galvanometer to control the heat supply sufficiently to keep the bridge near a balance and consequently the temperature near a fixed value. This was arbitrarily determined in advance by properly setting on the slide wire.

The controller galvanometer had mounted on its moving coil a thin glass crossarm in the end of which was sealed a bit of platinum wire, which was therefore capable of moving in a horizontal path through a short distance. Above and below this path were two platinum-faced jaws covering a half of the path. The jaws were closed periodically by clockwork. Should the wire happen to be between the jaws at their line

of closure a contact would be established and a relay energized which, short-circuiting an outside lamp-resistance in series with one of the inside heating coils, would thus increase the heating current periodically till the proper temperature of the bath would be re-established. Cooling of the bath was effected by loss of heat to the room which had to be at least 5° cooler.

The performance of this thermostat was very good, keeping the bath, under the best working conditions, constant to $0^{\circ}.001$; and in but few instances was the fluctuation more than $0^{\circ}.004$. Further it was remarkably convenient to set at any desired temperature.

The use of a 220 volt D.C. supply is perhaps open to criticism; but with care in insulation, trouble from this source was overcome. It was the only kind of power-supply at hand.

The Wheatstone Bridge:- Resistance measurements were made in terms of a decade resistance box manufactured by the Leeds and Northrup Co. of Philadelphia. The coils needed (from 30 ohms down) were calibrated twice, two years apart, and found to remain sensibly constant to well within the required accuracy. The nominal value of the ohm given by this box was not corrected in terms of a standard since only the relative values of the resistances are needed in thermometric work.

The thermometers on the high and low-pressure sides of the plug were connected into the bridge differentially as shown in Fig. 3, where

T_1 and T_2 represent the wires leading to the thermometer coils and C_1 and C_2 the compensation leads which will be described below.

The quantity desired is the difference in the effective resistances of the two thermometers. The Carey-Foster [28] method described in numerous text books therefore was employed because it measures directly the difference between rèsistances and eliminates all fixed contact-and lead-resistances. Its essential feature lies in the transposal of the resistances to be compared, which in this case are $T_1 + C_2$ and $T_2 + C_1$, but the means for effecting this transposal, namely a mercury commutator of special design, is omitted from the diagram. The method is too well known and the diagram would be needlessly complicated.

It will be noted that the arrangement of battery and galvanometer is not that usually published in the text-books. By putting, as indicated, the battery instead of the galvanometer in series with the sliding contact and by having no key in series with the galvanometer the error of thermal e.m.f.'s was eliminated. This arrangement is according to the practice of the Bureau of Standards at Washington, D.C. It has worked admirably and demonstrated the absence of any need of reversing the battery current.

The slide wire $S_1 L S_2$ is a "Students' Potentiometer" manufactured by W.G.Pye & Co. of Cambridge, England and consists of a wire wound in a helix on a slate drum and with sliding contacts $S_1 S_2$ at the ends. It has 10000 divisions from end to end and a resistance of 31 ohms approximately. This being too high for direct use it was shunted by a resistance of about half an ohm made up of manganin wire. With this arrangement and by repeated tests at different dates the value of one division was determined to be 0.00005666 ohms or, in terms of the particular thermometers used, equivalent to about 0.0005° C. The precise conversion of bridge readings into degrees will be given later.

The errors due to the variability of the contact resistances S_1 and S_2 being in series with as much resistance as 31 ohms, proved to be negligible - not over 0.12 of a division (or 0.00006° C) as found by a special test - while the nearest whole division only was read in the final temperature measurements. Thus the resistance of the sliding contacts were in series with 31 ohms and the whole shunted by 0.5 ohm, while all other junctions in the four arms were either soldered joints or amalgamated mercury contacts. Hence the only error due to the sliding contacts is a proportionate one on the basis of 31 ohms and therefore has proved negligible.

The wire $S_1 L S_2$ was calibrated several times and was found uniform to a small fraction of a division.

For resistance thermometry and with the battery connected between the thermometers as shown, the more sensitive arrangement is to have high-resistance ratio-arms; hence a high value of these, namely, 1000 ohms, was employed.

The key K_1 opened and closed the battery circuit while K_2 in conjunction with the resistance R , arranged to short-circuit a portion of the latter, permitted the observer to vary the battery current in the ratio $1 : \sqrt{2}$ and thus obtain quickly a correction for the heating effect in the thermometer coils of the measuring current. The smaller of the two values of the battery current was 6 milliamperes.

The Platinum Resistance Thermometers.

These were of the four-lead compensated type introduced by Callendar[29]. His method eliminates the uncertainty in the resistance of the leads by providing a duplicate pair of "compensation" leads parallel and close to the thermometer-leads in the region lying between the bath temperature and the room temperature so that the unknown but definite resistance of the one pair would be equal to that

of the other pair and being connected into adjacent arms of an equal ratio Wheatstone bridge, would thus automatically cancel in the measurement.

In the early forms the compensation leads, which were of coarser wire than the thermometer wire, were united directly at their ends. In later forms the ends were connected by a short length of the same kind of wire as the thermometer wire itself. This gave the added accuracy of compensating for the conduction of heat along the leads.

In the present experiments the thermometers were of this improved type. They were connected differentially into the bridge, thermometer No. 1 and compensating-lead No. 2, being connected in series on one side, while thermometer No. 2 and compensating-lead No. 1 were in series on the other side. These connections (Fig. 3) are lettered T_1, C_2 on the left - T_2 and C_1 on the right. In differential connections, the need for the compensation leads is very much reduced, but in the present instance, they were kept in to be on the safe side, especially in view of the fact that the depth of immersion of the two thermometers was not quite the same.

The wire for these thermometers was obtained from the Cambridge Scientific Instrument Co., Ltd., very pure and recommended by them

for thermometer work, in which they make a specialty. The diameter of the wire was about 0.03 mm., and its length such as to give a change in resistance of about 11 ohms for a change in temperature from 0° C to 100° C. It was wound upon the usual crossed mica frames in the form of a compact cube approximately 5 mm. each way. The fineness of the wire and the compactness of its mounting was for the purpose of allowing exploration of the space on the low-pressure side of the plug.

The leads were sealed into the ends of a glass tube as appears at T_1 or T_2 Fig. 4, and passed thence up the tube and out through a wax-sealed joint into the room whence they were connected to the bridge by heavy No. 14 lamp-cord about 3 meters long each. Only two leads are indicated in the diagram at the bottom.

The thermometer coils were exposed to the flowing air in some of the preliminary experiments, and later copper foil caps indicated by the dotted lines at T_1 and T_2 were slipped on. This made the galvanometer considerably steadier and did not introduce an objectionable lag because the copper caps should take the temperature of the gas before the walls of the enclosure.

The glass tubes containing the leads were enclosed in larger brass tubes of 1/8" pipe size (the brass tube for T_1 shown in the diagram is larger than natural size) which came in contact with the bath and

allowed air-connection to the differential manometer. The immersion of T_1 was about 44 cm. and that of T_2 about 34 cm. under the bath. The latter immersion was extended by a lagged air-space above the bath's surface by about 12 cm. This was thought sufficient to eliminate the effect of heat conduction along the leads inside the glass tubes in spite of the stagnant air-space by which the leads were surrounded.

Electrical insulation proved to have been amply provided for. Repeated tests of this were made; in fact, the bridge wiring was arranged so that the thermometer insulations between pairs of leads could be coupled in parallel and the combination thrown in series with the galvanometer and a battery of 30 volts. This test, as a matter of precaution, was made for nearly every run and in dry weather the galvanometer was not sensibly deflected, while in one or two instances in damp weather a film seemed to form on the outside insulation whose resistance was of the order of 20 megohms. This obviously would not affect the measurements.

Several tests were made for a possible effect of pressure on the resistance of the thermometers but none was found.

Callendar's formulae for the convenient computation of temperatures are:-

$$t_p = 100 \frac{R - R_0}{R_{100} - R_0} \quad \text{(defining the "platinum scale")} \quad .. (5)$$

and $t - t_p = \delta(0.01 \cdot t - 1) \times 0.01\, t$ (correcting to the hydrogen scale .... (6)

where δ is found by experiment, and for pure platinum has a value 1.50. This value as given by the Cambridge Scientific Co. for the specimen of wire purchased from them was accepted for the present investigation. As will be seen below the total correction introduced by the second relation would not exceed 1.5 percent of the observed temperature drop between 0 $^\circ$and 100°.

Thus, if Δt is a small temperature change, then from the second formula we get

$$\Delta t = \Delta t_p \left\{ 1 - \frac{2\delta}{10^4} (t - 50) \right\}^{-1}$$

$$= \Delta t_p \left\{ 1 + 0.0003 (t - 50) \right\} \quad .... (7)$$

to the first order of approximation where $\delta = 1.5$. The greatest value that the correction term can have between 0°and 100° is obviously 1.5%, and a small error in the corrective term would be negligible. For, as will be seeb later, the accidental errors in the determination of the Joule-Thomson coefficient are of the order of one percent.

The above correction was applied in the form

$$\mu = \mu_{tp} \left\{ 1 + 0.0003 (t - 50) \right\} \quad .... (8)$$

where μ_{tp} is the observed Joule-Thomson coefficient in terms of platinum degrees and μ is the same in terms of the gas-scale. (The distinction between the hydrogen and nitrogen scales need not be drawn for these measurements).

<u>The values of the fundamental intervals, i.e.</u> $R_{100} - R_0$:-

	Thermometer T_1	Thermometer T_2
May 12, 1915	10.952 ohms	10.930 ohms
" 14, "	10.963 "	10.932 "

Accurate knowledge of the fundamental interval of thermometer T_2 is all that is necessary, for that is the one whose resistance changes when the pressure drop is changed, the other thermometer on the high pressure side remaining constant at the temperature of the bath. The weighted mean for T_2 is

10.932 ohms.

The above tests were made with currents of air flowing past the coil at two speeds and with the air stagnant. No variation of consequence occurred.

As a further index on the stability of these thermometers, tests were made covering a year or more previously with ample constancy. These previous figures are not of use here, however, owing to necessary repairs to the compensation leads just before last tests were made.

Correction for heating due to current:- The bridge current, of course, heats to some extent the thermometer coils themselves and this must be allowed for. Since the liberation of heat is proportional to the square of the current, the resulting small rise in temperature should follow the same law. Callendar's method is to double the bridge current and subtract 1/3 the difference of the two settings from the first setting. The author found it a little more convenient to increase the bridge current in the ratio 1: $\sqrt{2}$. Thus the correction is immediately the difference in the two bridge settings.

Moreover, in order to make certain that this rule held under the present conditions a direct test was made with bridge currents in the ratio 1:2 : 2.5 : 4 . The linear relation between the bridge readings and the square of the current was satisfactory. This held also in varying currents of air. Thus where the rates of flow were 0, 2.9, 19, 36, 80, 132 and 250 cc/sec the corrected bridge readings were 0°.016, 0°.018, 0°.015, 0°.015, 0°.015, 0°.015, 0°.014 respectively (reckoning from an arbitrary zero).

The order of magnitude of the heating correction in the final runs was 0°.01.

Incidentally the above data show that there was no doubt as to the length of spiral being sufficient to give the gas the temperature of the bath.

Conversion of Bridge Readings to Degrees:- After this heating correction has been applied the differential reading may be converted into degrees by a multiplying factor which is obtained as follows:

The unit for reading off settings was taken as one revolution of the slide wire drum and is called the "bridge unit" hereafter. Repeated standardizations of the wire at four different dates in terms of the calibrated ohm gave the value

0.005666 ohms per bridge unit

Combining this with the figure just given of 10.932 ohms per 100° C we get the factor

0.05178 degrees per bridge unit.

Its four-place logarithm,

$\bar{8}.7142$,

is amply accurate for the present purpose.

Finally the factor given by formula (7) will convert to the gas scale according to the temperature, or formula (8) for the corresponding values of μ.

The porous plug. The form of plug finally adopted was suggested by Regnault[2] in the research already alluded to. The same principle has been published independently by Burnett and

Roebuck[30]. Its longitudinal section is shown in Fig. 4 by the dotted shading the material being earthenware - a pasteur filter. As may be seen, the flow of gas through the plug is radial toward an axis, and after passing through the plug wall its outflow takes place parallel to the axis. The purpose of this construction is to furnish thermal protection and obviously this can be done more thoroughly with this type than is possible with the straight-flow type of Joule and Thomson.

The whole arrangement (Fig. 4) is immersed in the bath whose surface is 44 cm. above the point T_1. Air, after traversing about 8 meters of pipe passes T_1 enters the plug casing at C and travels upward between the wall of the casing and a bright tinned radiation shield ssss, as is indicated by the arrows. After passing over the top of the radiation shield it fills the space immediately outside the wall of the plug through which it flows in two streams, divided by the "guard ring" gg. Within the plug is a glass tube t t which constrains the lower stream to pass, all of it, past the thermometer T_2 while the upper stream is kept from passing the thermometer. Both streams pass out finally at the top.

The purpose of the guard ring is to avoid errors arising

from conduction of heat along the material of the plug from its mounting FF and ultimately reaching the thermometer inside.

The temperature of the plug in general is different from that of the casing. Radiation between the two would introduce an error. The radiation shield is to prevent this. As will be seen later, the radiation shield is unnecessary but it is retained as a precaution, and the presence of a single shield is free from objection.

The construction of the plug casing (Fig. 4) permits the use of the principle of interchangeable parts. It may be seen there that different plugs may be bolted in and different sizes of casing as well. This proved a valuable feature in the preliminary experiments.

Fig. 5 shows a view of the plug-casing worm and the thermometer stems T_1 and T_2 . C is a double-walled can insulated with asbestos. Its purpose was to extend the immersion of T_2 above the level of the bath BB (which is about 90 cm. above the table). A indicates the level of the top of the bath cover with its insulation and AB gives an idea of the thickness of the cover of the bath. II shows the interchanger already described.

Fig. 6 shows a general view of the apparatus exclusive of the compressor. In the foreground is a steam boiler for jacket heating which was not used. Next is the bath situated within the legs of a work-

table upon which are fastened switches, stirrer, motor and manometers, the latter fastened to the tall board at the rear. In the background at the right is the telescope for reading the manometer, and at the left are the bridge and thermostat galvanometers. Under these is a table upon which rest the bridge and accessories. The cables leading to the bridge from the thermometers are seen overhead and dropping down to the bridge proper which is covered. Under this are the ratio-arms and the Carey-Foster commutator; in front is the slide-wire.

Preliminary Experiments.

Early Experiments with straight-flow Plug:- A number of experiments were carried out at the Johns Hopkins University in 1905-6, on carbon dioxide with a straight-flow plug of the type used in the Joule-Thomson experiments. Platinum resistance thermometers were used and so arranged as to be movable. The pressure-drops were of the order of one atmosphere. Plugs of various materials were tried, eider down, cotton, silk and paper. A vacuum-jacket was attempted and, what seemed better, the guard ring principle contained in a suggestion by Buckingham[31] was carried out. The porous plug was concentric with a second annular plug designed to eliminate lateral temperature gradients.

The last arrangement improved things somewhat, giving one result in agreement with those of Joule and Thomson, but the general characteristic of the experiments was their lack of reproducibility.

On displacing, for instance, the low-side thermometer a strange temperature gradient was observed. The observed cooling effect continually fell off as the thermometer receded. A shift, for instance, from 1 to 4 and 6 cm. distances cut the effect to about 1/2 and 1/3 respectively!

With varying rates of flow also the effect varied, but with a tendency toward a limit for the higher speeds. Natanson observed a variation with flow also. Perhaps we can thus account for the partiality of observers for high flows and plenty of gas.

In addition an erroneous amount of time had to be consumed before a steady state could be attained, amounting to an hour and a half before a reading for a single point could be taken. Apart from other considerations this would lead to a large chance for error unless the pressure regulation were watched very closely. A damped oscillation in the cooling-effect similar to that in the Joule-Thomson experiments was also observed.

It was decided, then, as already mentioned, to concentrate on the method and to narrow the field to the attainment of reliable

results. What was to be desired was thermal protection, a fine pressure regulation, and good temperature control. These have been attacked in a manner already taken up in the description of the final apparatus. They have been carried out in the Rouss Physical Laboratory of the University of Virginia.

Later Preliminary Experiments with Radial Flow Plug Exploration.

Referring to Fig. 4 it will be remembered that the thermometer T_2 was capable of being shifted throughout the entire length of the plug. In the initial explorations the inner tube tt had not been introduced. The temperature distribution was fairly uniform except above the middle, and the correction for the heating of the thermometers due to the bridge current was much larger at the bottom of the plug, where the air-flow was slow, than at the top. The introduction of the tube and guard ring not only reduced this correction to be applied but rendered the temperature distribution along the tube uniform to the order of $0^\circ.001$. Closer tests than this were not pressing nor possible for the time-fluctuations due to bath and pressure fluctuations were of this order of magnitude.

Rate of Flow:- This was separately measured by collecting the gas over a pneumatic trough. Roughly the linear speed was found to be directly proportional to the pressure drop and independent

of the absolute pressures, and hence of density. The result can therefore be simply expressed by a single number, namely 2.3 cm. per sec. per cm. drop of mercury. In the final runs this would mean a maximum speed within the tube tt of 180 cm. per sec., a little more than this at the bottom of t t and about double this around the thermometer caps. In the spiral leading into the plug-housing , the speed was about the same.

"Velocity cooling".- The upper limit of the possible errors arising from the change in kinetic energy involved in the above variation of speeds was computed to be of the order of magnitude of 0°.004 C. Actually none was observable. For, in a run with the plug removed and with speeds of flow in the ratios 50:100:200 :330 the bridge readings in terms of an arbitrary zero were 0°.037, 0°.038, 0°.038, 0°.038 respectively. The fastest flow exceeded the limit for the final runs. This run was taken with the thermometer caps on when the error from velocity cooling should be a maximum as is plain from a glance at Fig. 4. For when the caps are removed the speed of air past the thermometer coils would be less.

Effect of Varying Rates of Flow upon the Observed Temperature Drop.

These observations are depicted graphically in Fig. 7. Curve 2 was taken with the plug whose characteristic rate of flow has just been given, namely 2.3 cm. per sec. per cm. pressure drop. Curve 1

applies to the same plug wrapped with rubber bands till its characteristic flow was 0.7 as great, while curve 3 is for a plaster of Paris plug whose flow was 3 times as great.

The first essential feature of these curves is that they are straight lines within the error of experiment except near the origin. (This is true not only in the preliminary but in the final runs) Here the points were so irregularly distributed that they have been omitted from the diagram. The cause may have been that with the very slow flow of gas, the steady state may not have been reached, or, what is more probable under these conditions some slight heat leakage produces relatively larger temperature errors near the origin.

The latter cause, heat leakage, evidently applies in regard to the second essential feature, namely that the more rapid the flow the nearer the curve approaches to the ideal of passing through the origin.

A third feature is that these lines are sensibly parallel, which will be taken up later.

Heat leakage by conduction:- The nature of this heat leakage was sought in conduction, radiation and convection. Conduction through the gas does not seem probable. The only remaining path would be along the material of the plug. This point was tested by shifting the guard-ring from a position 1.5 cm. from the plug flange FF

(Fig. 4) to a point 5.5 cm. therefrom. The results as shown by the rings and crosses (Fig. 7) rule out this source of error, the curves (No. 2) in these two cases being indistinguishable.

Heat leakage by radiation:- Since the surface of the plug must be at a different (lower in case of air) temperature from that of the walls of the plug casing, heat may pass by radiation across the annular space between them and thus reach the interior without being absorbed by the gas itself, and so an error may be introduced. This was first tested by comparing runs with the dark iron casing walls lined with bright tin and then without the tin. There was no systematic difference. Again a trial was made with 3 radiation shields on the one hand, disposed as in Fig. 8, in a large casing and on the other with no radiation shields at all, the casinghappening to be that shown in Fig. 4. Fig. 9 shows that these results too are indistinguishable. Radiation, then, is not to be looked for to explain the depression of these lines nor as a serious source of error.

Heat leakage by convection:- A turbulent motion of the gas surrounding the plug could convey heat across from the walls of the casing by a sort of to- and fro motion without permanent absorption. If so an increase in the inside diameter of the casing should reduce

this error and shift the lines nearer to the origin. Now in the experiments of Fig. 9 (no shield), the space between the walls and the plug was about 6 mm. thick about twice as thick as for the experiments of Fig. 7. The curve of Fig. 9 passes much nearer to the origin. Consequently convection must play a part.

It was not thought worth while to push these experiments further, the practical limit being apparently reached in the experiments of Fig. 9.

Effect of density on the approach to the origin:-

For greater densities and consequently greater volumetric thermal capacity it would be expected that these curves would pass nearer the origin. This is borne out by the curves of Fig. 10 as well as by the results of the subsequent final runs (of which these are the first). These curves have different slopes too, but that is an independent matter to be discussed presently.

Derivation of the Joule-Thomson Coefficient μ

Under the head "remarks on theory" it was pointed out that μ is equal to the slope of the tangent to a curve H = const. in the t-p plane.

Now considering the type of curves plotted in Figs. 7,9 and 10, each curve may be considered as made up of two portions, the

larger being rectilinear, a smaller, curvilinear (not drawn), connecting the lower end of the other with the origin. Now, by considering experiments carried out at successively increasing absolute pressures, it should be possible to construct curves representing the integrated effect over a wider range of pressure drops than is carried out in these experiments. This curve should be a smooth curve. With the former portion it is possible to do this, with the latter impossible; and being in addition non-reproducible the latter portions are meaning less and so are rejected.

Confining ourselves, then, to the straight portions it seems highly probable that if we could take a high value of the density and hence of volumetric thermal capacity and then increase the rate of flow indefinitely we should get a series of parallel straight lines whose limit would be a single parallel straight line passing through the origin. This inference is based on results such as are depicted in Figs. 7,9 and 10.

The slope of this limiting line would then be the true value of μ. Therefore the slopes of the actual lines would give very near, if not actually within the ordinary accidental errors of observation, the true values of μ. Further these lines pass so near the origin under the final conditions that an oversight of this point would not

introduce a very great error (Figs. 9 and 10) say 4 to 6 percent taking their extreme points and the origin.

Looking at the matter from a little different point of view it appears that the thermal leakage is a constant quantity, else the change in the rate of flow would change the slopes of the lines as well. Now the variation in H would be measured by the variation in this leakage. If so then, the straight lines are lines of constant H. Further, any residual variation in H is minimized relatively with the increased rates of flow characteristic of the portion of the diagram removed from the origin. It must be admitted, however, that there remains a difficulty in explaining this apparently constant heat leakage.

Another bit of corroborative evidence may be mentioned here. From Fig. 10 it will be noted that at the higher absolute pressures the lines are flatter. Hence an integrated Joule-Thomson effect extended over a fairly wide range would be represented by a curve concave downward. This curvature, however, is too slight to be noticeable in the limited range of pressure-drop in a single experiment. Now the same type of curvature is obtained by Dalton (loc. cit.) in curves computed for hydrogen from the empirical isothermal of

Kamerlingh Onnes, and applied to all gases by the law of corresponding states.

Values for the absolute pressures and temperatures:- Following upon what has been said under "remarks on theory" the appropriate absolute temperature and pressure to select are obviously those of the mid-point of the limited straight lines of the diagrams Fig. 10. The temperature drop in degrees is so slight that the temperature of the bath was kept uncorrected.

Zeros of the differential thermometers:- Since the slope is all that is needed the determination of the zero, i.e. for pressure-drop = 0, was not required. At best these are uncertain, for in the present apparatus the determination should have to be made in stagnant air, moreover a long time is required. Hence, after the experiments (Fig. 10) zeros were no longer determined.

Effect of moisture:- This was not very great by test, thus the following figures were obtained.

With long-used calcium chloride,	μ = 0.35	degrees	per	meter
" no drying materials	μ = 0.34	"	"	"
" new calcium chloride	μ = 0.33	"	"	"

It here appears that the old materials were worse than none and that in the final experiments, the drying with phosphorus pentoxide was sufficient. It was used in all except those at 20°C, and there is no

indication of an error from this cause there.

Final Experiments.

Between the months of August 1915 and January 1916 fourteen values of the Joule-Thomson coefficient were measured. These accord very well with a general formula as will be shown presently and this is taken as an index of their reproducibility.

Table I is a specimen of a single day's observations. It will be noticed that the bath temperature was read on a thermometer standardized by the Physikalische Technicheche Reichsanstalt. The corrections were too small to be needed. The barometer readings were taken for the purpose of finding the absolute pressures of the experiment. The test for bridge leak was omitted, by inadvertence, on this day. Dry days, however, uniformly were days of no leak. This omission is exceptional nevertheless.

Column No. I gives the time of the observation. It will be noticed that the steady state is obtained in a relatively short time. Each point is computed from the observations in a single horizontal row, set off by the horizontal lines. Column No. 2 shows the performance of the thermostat as read on a Beckmann thermometer. The jacket temperature recorded in Column 3 is of minor importance and refers to the temperature in the air space

Expt No 24 | High side pressures 6.832 m. 9.0 atm. | Barometer 594.2
Date - Dec 1, 1915 | Mean pressure 6.330 m. | 164.0 / 758.2
Bath temp. rdg 49.98 P.T.R. | Bridge leak Not tested. dry day. | temp cor. -3 / 755

(1) Time h m.	(2) Thermostat	(3) Jacket t	(4) Rm t	(5) Gauge Wts	(6) Manometer Left	micr	(7) Right	micr	(8) Bridge R o √2 2.	(9) B o √2 2	(10) B-R. dirs	(11) Δp mm.	Remarks.
10 33	5° 129	33 5	20.6 / 19 2	118	868.6	1.00 / 1.73	75.1	-14.93 / +1.25	48 .79 .66	52. .35 45	3.32	793.5 / - 2.7 / - 0.7	Very steady Power occasionally slacks for 4 or 5 sec
									.81 .67	35.47			
									.79 .66	.34 .48			
	.127			118	868.7		75.2		.78 .66	.37 47			Pentoxide white
				5820g.					.79 .66	.35 .47			
					Meniscus 0.73		Meniscus 1.32		48.92	52.24		790	
11 17	.120			118	829.3	0.54 / 1.32	115.9	1.00 / 1.87	48 .61 44	52. .55 .70	3.70	713.4 / - 2.4 / -0.2	
									.62 49	.56 .68			
									.60 .46	.55 69			
11.37	.124			117.5					.57 .45	.56.68			Steady pressure Manometer set on cross-wire and remained
				5800g.	829.3		115.9		.60 .46	56 .69			
						0.78		0.87	48.74	52.44		711	
12.00	.124		Mean 21°.1	118.5	639.4	0.48 / 1.46	332.1	0.51 / 1.20	47 .53 .42	53 .60 .71	5.86	307.3 / -1.0 / +0.3	
									.52 42	.61 .71			
									53 .42	.61 .72			
23	.126			5900g.					.54 42	.60.71			
									53.42	.60 71			
					639.5	0.98	332.2	0.69	47.64	53.50		307	
12.53				120	588.8	1.22 / 1.76	394.9	1.09 / .92	47 18.09	53. .84 .94	6.46	193.9 / - 0.7 / - 0.5	Power off and fresh start necessary before beginning this set. Power variable Settled down during last half of observations
									21.09	.85.94			
				5950g.					.20 .12	.85.96			
1 20	.127								.23 .13	.90.98			Pentoxide white and beginning to get gummy
					588.8		394.9		20.5 .11	.86 .95			
		34.8	23.1 / 21.6			0.54		0.83	47.30	53.76		193	

5900 g.
3% 177
Bar 755
6.832 meters — high side
− .500
6.332 " mean.

Table 1.

space surrounding the bath. The room temperature in Column 4 was for the particular purpose of reducing the manometer readings to $0^{\circ}C$. The thermometers were close to the manometer. In Column 5 are given both the readings of the dial gauge and the piston gauge communicating with the high pressure side of the plug. At the bottom is the computation reducing the piston gauge readings to meters of mercury (6.832) and also computing the mean pressure of the experiment (6.332). Columns 6 and 7 give the readings on the manometer measuring the pressure difference between the two sides of the plug. In this the height of the meniscus is taken as well. The double underscored numbers are the final values of the readings on the manometer computed from the telescope settings. Columns 8 and 9 contain the record of the bridge settings for measuring the temperature drop, two columns being needed for the transposings of resistances characteristic of the Carey Foster method. The whole numbers under R and B are the bridge readings as far as the unit revolutions of the slide wire drums go and the numbers following are the fractions thereof. A unit, in the last place corresponds to approximately $0\overset{\circ}{.}001$ in the same column. The numbers $0, \sqrt{2}, 2$ refer to the ratios of the bridge currents. By taking the difference of the means under $\sqrt{2}$ and 2 the correction for the heating effect of the bridge current is obtained,

which applied to the mean under $\sqrt{2}$ gives the computed setting for zero current - a process already explained. This computed value is found at the lower left hand corner of each block of bridge settings. The number in parenthesis between the two columns is simply a check obtained by adding up the two readings as above corrected, and corresponds to the mid-point of the bridge. It should be practically a constant. The variations exhibited correspond to a maximum of 0°.002. Column 10 gives the difference in temperature expressed not in degrees but in the slide wire readings. The approximate value of a unit in the last place is 0°.00050 . The reduction to degrees need not be made until after the Joule-Thomson coefficient is calculated in bridge units. Column 11 gives the calculated value of the pressure drop with the corrections for temperature and capillarity applied respectively. The column headed Remarks does not call for special mention except perhaps in regard to the phosphorus pentoxide. It will be noticed that the pentoxide remained white except near the end of the experiment. This is taken to indicate that the air has been reasonably dry for the purposes of the experiment. The pentoxide was placed in a drying tube provided with a glass window for constant inspection during a run.

Calculation of the Joule-Thomson Coefficient.

In Table II are assembled the reduced observations of the different experiments, with dates, bath temperatures and pressures in the first three columns. The pressure is a mean value computed in accordance with the procedure already explained. Column 4 gives the pressure drop reduced to $0^{\circ}C$ and corrected for capillarity. The bridge readings are given with reference to an arbitrary zero since, for reasons given above the slope of the graphs of pressure-drop and temperature drop are all that are needed. The measurements at 30°, however, are an exception, the zeros there being carefully determined. Fig. 10 is plotted from these observations. The intercepts on the temperature axis (column 10) therefore are known to their absolute value only in this group. Their progression shows numerically the closer proximity to the origin of those lines taken at the higher pressures. In the remaining groups, the intercepts are known only to an additive constant, but this progression is repeated except for the last intercept.

Columns 6,7 and 10 are calculated from these observations by the method of least squares kindly done under the direction of my colleague Dr. S. A. Mitchell, Professor of Astronomy. The slopes (column 6) when reduced to degrees will be the adopted values of the Joule-Thomson coefficient.

Table II.

1 Date	2 Bath temp.	3 Pres-sure (meters)	4 Pressure drop (meters)	5 Bridge readings	6 Slope (Bridge units per meter.	Residuals 7 Bridge units	 8 degrees	9 Wt.	10 Inter cepts.
1916									
Jan.10	15°.9	2.45	.763	-14.26	0.698	-	-	0.2	
			.260	-10.75					
"		2.65	.694	-13.53	0.622			0.3	
			.263	-10.85					
1915			.792	4.67		-0.01	-0.0005		
Aug. 20	30°0	2.49	.599	3.48	0.635	+0.02	+0.001	1.0	-0.34
			.311	1.63		0.00	.0000		
			.241	1.18		-0.01	-0.0005		
			.697	3.98		-0.01	-0.0005		
" 23	"	4.48	.631	3.59	0.607	0.00	0.0000		
			.298	1.60		+0.03	+0.0015	1.0	-0.24
			.199	0.94		-0.03	-0.0015		
			.726	4.07		-0.01	-0.0005		
" 26	"	6.40	.620	3.46	0.588	-0.02	-0.001	1.0	-0.19
			.310	1.63		0.00	0.0000		
			.255	1.32		+0.01	+0.0005		
			.747	4.12		+0.02	+0.001		
			.653	3.54	0.560	-0.03	-0.0015	1.0	-0.08
Nov.24	50°.0	2.50	.343	1.84		+0.01	+0.0005		
			.264	1.39		0.00	0.0000		
			.820	4.37		-0.05	-0.0025		
Nov. 29	"	4.50	.689	3.77	0.535	+0.05	+0.0025	0.5	+0.03
			.309	1.71		+0.03	+0.0015		
			.193	1.03		-0.03	-0.0015		
			.790	4.28		-0.02	-0.001		
			.711	3.90	0.529	+0.02	+0.001	1.0	+0.12
Dec. 1	"	6.33	.307	1.74		0.00	0.0000		
			.193	1.14		+0.01	+0.0005		

Table II. continued.

1 Date	2 Bath temp.	3 Pressure (meters)	4 Pressure drop (meters)	5 Bridge Readings	6 Slope (Bridge units per meter)	Residuals 7 Bridge units	8 degrees	9 Wt.	10 Intercepts
1915									
			.769	3.93		+0.02	+0.001		
Dec. 6	70°0	2.53	.500	2.54	0.496	-0.04	-0.002	1.0	+0.1
			.259	1.41		+0.02	+0.001		
			.747	3.84		-0.01	-0.0005		
Dec. 8	"	4.36	.497	2.66	0.480	+0.01	+0.0005	1.0	+0.26
			.247	1.44		-0.01	-0.0005		
			.718	3.72		0.00	0.0000		
Dec. 13	"	6.40	.498	2.70	0.468	+0.01	+0.0005	1.0	+0.36
			.255	1.55		0.00	0.0000		
			.746	4.87		0.00	0.0000		
Dec. 16	90°0	2.44	.509	3.83	0.441	0.00	0.0000	1.0	+1.57
			.257	2.71		0.00	0.0000		
			.747	4.91		-0.01	-0.0005		
"	"	4.52	.495	3.88	0.421	+0.02	+0.001	1.0	+1.78
			.248	2.81		-0.01	-0.0005		
			.743	3.51	0.406	-0.02	-0.001	1.0	+0.51
Dec. 15	"	6.35	.506	2.60		+0.04	+0.002		
			.253	1.52		-0.02	-0.001		

Especial attention is directed to column 8 which shows the deviations from the linear relation of the observed temperature-drops. Their order of magnitude is seen to be 0°.001 C although some are greater and some less. Their algebraic signs occur in haphazard order yielding no indications of curvature within the given limits of pressure drop.

The observations dated Jan. 10, 1916 at 15°.9 were made under such difficult conditions that the number of observations obtained were insufficient for a least square reduction. Hence their weights (column 9) were given a low value. All the other weights were given the value unity except for the observations of Nov. 29, 1915 which was reduced owing to temporary defects in the pressure control.

A uniformly diminishing value of the slope (column 6) with increasing pressure (column 3) is to be noted. These variations are linear within experimental error. The diminution with increasing temperature is not linear. (Fig. 11).

<u>The Joule-Thomson coefficient as a function of temperature and pressure.</u>

The value of μ in bridge units was converted into degrees on the platinum scale by the multiplying factor 0.05178 (log. = $\overline{8}$.7142) given on p. 33 and then to the gas scale by formula (8) p.30

These fourteen reduced values are arranged in Table III in rows and columns corresponding to approximate pressures and temperatures respectively. The precise values of the pressures are in Table II. The

residuals will be explained presently.

Now since μ is linear in p and not linear in t, the natural interpolation formula to try first, is one of the first degree in p and the second in t. This would involve a formula of five constants. A least square computation of these constants done again under Professor Mitchell's supervision gave:

$$\mu = +0.3935 - 0.00691\, p - 0.001835t + 0.00000134t^2 + 0.0000325pt \quad \ldots(9)$$

where μ is expressed in degrees per meter of mercury

p " " " meters of mercury

t " " " degrees Centigrade

Five constants are too many for so short a range and only fourteen points. Resort then was had to the three-constant formula already developed under "Remarks on Theory". A least square reduction for this carried out by my associate Professor Sparrow and myself, yielded

$$\mu = -0.2599 + 181.96\,\frac{1}{T} - 552.42\,\frac{p}{T^2} \quad \ldots\ldots\ldots\ldots\ldots (10)$$

where $T = 273^{\circ} + t$.

The manuscript for these computations has been preserved. They are too long and complicated to make worth while their presentation. Numerous checks were applied throughout the work, and the smallness of the residuals constitute an index of accuracy.

Table III.

The Joule-Thomson coefficient as a function of temperature and pressure

Approximate pressure. (meters).	15° C	30° C	50° C	70°C	90°C.
2.50	.358 +.008 +.002	.327 +.002 +.001	.290 -.002 .000	.258 -.002 -.001	.232 +.002 +.001
4.50		.312 -.001 -.002	.277 .000 -.002	.250 -.001 .000	.220 -.001 -.002
6.40	.319 -.006 -.010	.302 .000 .000	.274 +.002 +.004	.244 +.002 +.003	.213 -.001 -.002

Upper line of residuals ..... five-constant formula

Lower line of residulas ..... three-constant formula.

The residuals in Table III are μ-observed minus μ-calculated and are arranged under μ-observed. The upper residual in each case is that due to the five-constant formula, the lower to the three-constant formula.

The five constant formula naturally comes closer to observation but there is not much choice. The average residual is rather under one percent.

Comparison with other formulae:- The formula given by Joule and Thomson (loc. cit) for air is

$$\mu = 0.92 \left(\frac{273.7}{T} \right)^2 \quad \text{per 100 in of mercury}$$

$$\text{or} \qquad \mu = 0.363 \left(\frac{273.7}{T} \right)^2 \quad \text{" meter " "}$$

At the ice point this would amount to

0.363 degs. C. per meter;

whereas the formulae of this paper give

$0.3935 - 0.00691\ p.$

The results are comparable only if the pressure is specified in the latter case. Thus at 4.4 meters, or 7.3 atm. both numbers agree. This even is not strictly comparable on account of the large pressure drops

(5 or 6 atm.) of the Joule-Thomson experiments. Further it is interesting to note that by integrating my formula above between the limits of 11 and 1 atmosphere approximately again the two numbers would agree.

The formula of Rose-Innes (loc. cit.), reduced to meters per degree, is

$$\mu = - 0.275 + 173.8 \frac{1}{T}$$

It is based on the Joule-Thomson observations and fits them better than the original formula of the two experimenters having two constants. It is the same in form as the first two terms of the three-constant formula (10).

The only other formula which has been proposed is that of Noell (loc.cit) already recorded p.5. Where the two overlap it is in fair agreement with that of Joule and Thomson. Comparing his pressure coefficient at $0^{\circ}C$ with mine we have respectively -0.0015 as against -0.0069 in degrees and meters. The two thus, at least, have the same sign and if mine were computed on the basis of pressure drop of 6 to 10 atmospheres the agreement would be better, at least in the absolute values if not in the pressure coefficient. It is of interest to note here that the pressure coefficient of Natanson for carbon diox-

ide is positive and that his value is not in agreement with Kester's. One would expect, by the law of corresponding states and the fact that the pressure coefficient is independent of temperature and pressure, that it should be of the same sign for all gases.

Theoretical Deductions.

Owing to the limited range of pressure and temperature in these experiments and to the fact that only one gas, and that a mixture, has been experimented upon there is naturally a limit to the extent of these deductions. Further, it would be advisable to give more definite values to the present data by additional observations, but, of course, one always feels that way about any piece of work; interesting conclusions, however, may be drawn from the experiments so far performed.

There are two general fields for these, the attainment of the thermodynamic scale and the question of the internal energy of a gas as a function of specific volume particularly. Bound up with these is, of course, the form of the characteristic equation and incidentally the variation of C_p with temperature and pressure.

The last point will be taken up here, as well as a consideration of the first subject.

Calculation of the temperature of the ice point on the thermodynamic scale : - The general relations are

$$\frac{v_{100}}{T_{100}} - \frac{v_o}{T_o} = \int_{T_o}^{T_{100}} \frac{\mu C_p}{T^2} dT \qquad \text{(pressure = const)} \ldots\ldots(11)$$

$$v_{100} = v_o (1 + 100 a) ,$$

$$T_{100} - T_o = 100$$

The first is one of the two ways of integrating equation (2), the second gives the experimental determination of the mean temperature coefficient at constant pressure, a, while the last is a definition. The limits of integration are the two temperatures of the ice point and the steam point.

Factoring out a mean value of c_p which varies but slightly within these limits, calling it $\overline{C_p}$; calling the value of the remaining definite integral ($I_{100} - I_o$) and noting that $\frac{1}{v_o} = \rho_o$ the density of the gas at the given constant pressure and at the ice point; the combination of these three relations results in

$$T_o = \frac{1}{a} + \frac{T_o(T_o + 100)}{100 a} \rho_o \overline{C_p} (I_{100} - I_o)$$

without approximation.

The last term on the right is a small correction term and approximations not less than the percentage accuracy of $I_{100} - I_o$ i.e. of the order of one percent are admissible. But, since putting $T_o = 273$ involves

errors of but one tenth this amount, we may then have

$$T_o = \frac{1}{a} + \frac{273 \times 373}{100\, a} \times \rho_o\, \bar{c}_p\, (I_{100} - I_o) \quad \ldots\ldots\ldots\ldots (12)$$

Now a has been determined with great accuracy by Chappius[32] to be

$$0.00367282 \ \text{degs}^{-1}$$

at one meter of mercury, the standard thermometric pressure. From this

$$\frac{1}{a} = 272.^\circ 270$$

ρ_o at one meter of mercury is $.001293 \times \frac{100}{76}$

The data for $\bar{c}_p$ vary considerably. The most recent determination is by Swann[33] working in Professor Callendar's laboratory. He found values 0.2417 and 0.2430 cal. per gm. per deg. at 20° C and 100°C respectively. A mean value of

$$\bar{c}_p = 0.242 \text{ cal. per gm. per deg.}$$

is adopted here.

To convert this into mechanical units the mean value adopted for the mechanical equivalent of heat is

$$4.18 \times 10^7 \text{ ergs per cal.}$$

The value of $(I_{100} - I_o)$ comes out

+0.000306 by the three-constant formula for μ

and +0.000308 " " five-constant formula for μ.

where the pressure unit is the meter of mercury. So convert this into dynes per sq. cm. the value chosen for the density of mercury and the value of g are

13.595 gm. per cm^3 and 980 cm. per $sec.^2$ respectively.

[The value of g determined here by the U.S. C.G.S. is 979.937 cm. per $sec.^2$]

From these data are obtained the correction terms to (11) viz:-

$1.^\circ 091$ by the three-constant formula

$1.^\circ 098$ " " five- " "

or, for the absolute zero:-

$\underline{\underline{273.^\circ 36}}$ by the 3-constant formula

$\underline{\underline{273.^\circ 37}}$ by the 5-constant formula.

The other determinations of most recent date are by Buckingham (1908) using the Joule-Thomson coefficient for various gases adjusted into a single reduced formula by the "law of corresponding states", and by Berthelot (1907) using the characteristic equation. Previously in 1903 he had computed values on the basis of the Joule-Thomson effect.

Collecting these results we have for T_o :-

Author	T_0	Gas	Method	Source
Buckingham (1908)	273.273	Air	J-T effect	Buckingham's paper[24] (1908)
	273.286	N_2	"	"
	273.049	H_2	"	"
	273.267	CO_2	"	"
Berthelot (1903)	273.13	H_2, N_2, Co_2, Air	"	"[24] (1907)
Berthelot (1907)	273.04	H_2 in Pt-Ir(1)		Berthelot[25] (1907)
	273.07	" " " (2)		
	273.10	" in verre dur		
	273.09	N_2		

It will be noted that my result is higher than these; and that of these Buckingham's calculations are higher than those of Berthelot. How Berthelot could obtain so low a value using previous values of the J-T effect I am at a loss to explain, not having seen his calculations. It will be noted that hydrogen gives the most uncertain results.

A possible explanation for the behavior of hydrogen that has been advanced by Berthelot and by Rose-Innes and perhaps others is that there is some surface action or condensation between hydrogen and the walls of the thermometric vessel. This would effect a. Possibly then the main term, $\frac{1}{a}$, and not the correction

term may be at fault. Hydrogen, it may be observed, seems to do better in <u>verre dur</u> than in platinum iridium.

This surface action is a possible explanation of the discrepancies in all the gases. In my own experiments the only error I can think of that has not been directly tested for is that arising from heat conduction along the thermometer leads. If found by direct test, a correction factor can be determined and applied to the present data on μ. It is proposed to do this and in addition to repeat the runs with thermometers of a different design.

Finally it is noteworthy here that an accuracy of one part in 27000 for α is necessary as against only one part in 100 for μ.

<u>Corrections to the constant-pressure air thermometer between the ice and steam points</u>:- Here we shall find a much closer agreement between my results and the calculations of others, as is to be expected.

Let t' and t be the centigrade temperatures on the constant pressure scale and on the thermodynamic scales respectively and T' and T the same temperatures referred to their respective absolute zeros, so that obviously $T' = T'_o + t'$ and $T = T_o + t$; let $t' - t = \epsilon$, the correction sought, and let finally η = the corrective term in

equation (12), i.e. the correction, $T_o - T'_o$ which must be added to T'_o to get T_o. Then it follows that

$$\epsilon = -\eta \frac{t}{T_o} + T_o T'_o \; \rho_o \bar{c}_p \; (I_T - I_o)$$

where the $I_T - I_o$ has the same significance as before, the upper limit being variable in the case of I_T. Now making again the same approximations and remembering that $T'_o = \frac{1}{a}$, we get the final result

$$\epsilon = \frac{\rho_o \bar{c}_p}{\alpha} \left\{ (t + 273) (I_T - I_o) - 3.73 \, t \, (I_{100} - I_o) \right\} \qquad \ldots(13)$$

an equation kindly put in this form by my associate Professor Sparrow.

Corrections calculated by this formula for every 10°C are to be found in the last column of Table IV attached to a table copied from Buckingham's [24] article in the Phil. Mag. (1908). The new values and those of Berthelot in this instance are seen to be practically identical. Chappius (loc. cit.) moreover states that the air and nitrogen scales are sensibly the same in this interval; so that we have here a real basis for comparison. This is agreement within the accuracy of gas thermometry.

Table IV.

THERMODYNAMIC CORRECTIONS TO THE CONSTANT PRESSURE NITROGEN SCALE OBTAINED BY VARIOUS WRITERS, COMPARED WITH THE CORRECTIONS TO THE CONSTANT PRESSURE AIR SCALE DEDUCED FROM THE JOULE-THOMSON EFFECT. 1000 mm. = pressure.

t°C.	Rose-Innes 1901	Callendar 1903	Berthelot 1903	Buckingham 1907	Mean	Hoxton(Air) 1916
10	0.0120	0.0109	0.010	0.0078	0.010	0.0100
20	0.0205	0.0188	0.017	0.0137	0.017	0.0170
30	0.0261	0.0236	0.022	0.0179	0.022	0.0212
40	0.0288	0.0260	0.024	0.0203	0.025	0.0235
50	0.0289	0.0260	0.024	0.0209	0.025	0.0238
60	0.0269	0.0240	0.022	0.0198	0.023	0.0218
70	0.0228	0.0204	0.019	0.0172	0.020	0.0189
80	0.0168	0.0151	0.014	0.0129	0.015	0.0141
90	0.0092	0.0081	0.007	0.0071	0.008	0.0068

Variation of c_p with pressure:- Recent work of Holborn and Jacob[34] on c_p for air at 60° C and at pressures from 1 to 200 atmospheres affords a further comparison of the present work with that of other observers in that the Joule-Thomson effect can be ultilized to evaluate the pressure coefficient.

Writing equation (2) in the form

$$\mu\, c_p = T \left(\frac{\partial v}{\partial T}\right)_p - v$$

and differentiating with respect to T at constant p , we get

$$\mu \left(\frac{\partial c_p}{\partial T}\right)_p + c_p \left(\frac{\partial \mu}{\partial T}\right)_p = T \left(\frac{\partial^2 v}{\partial T^2}\right)_p = - \left(\frac{\partial c_p}{\partial p}\right)_T \quad ..(14)$$

the last member following directly from an independent well-known equation.

Now the left hand member can be evaluated by using either formula for μ and Swann's values (loc. cit) of c_p and $\left(\frac{\partial c_p}{\partial T}\right)_p$. Note that in regard to units c_p may be expressed in calories per gm. per deg. since the equation is homogeneous in that physical quantity. Also since μ is here expressed in degrees per meter of mercury and since the data of Holborn and Jacob for $\left(\frac{\partial c_p}{\partial p}\right)_T$ are expressed in atmospheres for the pressure unit, the left hand member must be multiplied by

0.76 to make the two sets of results comparable. Finally T must be put equal to 273 + 60 = 333, the temperature of Holborn and Jacobs' experiments.

Now Swann gives at one atmosphere,

$$c_p = 0.241 \quad \text{and} \quad \left(\frac{\partial c_p}{\partial T}\right) = 0.000016$$

then by the 3-constant formula (10) also at 1 atmosphere

$$\mu \left(\frac{\partial c_p}{\partial T}\right)_p = \left(0.2599 - \frac{181.96}{333} + \frac{552.46 \times 0.76}{(333)}\right) \times 0.000016$$

$$= 0.0000047$$

$$c_p \left(\frac{\partial \mu}{\partial T}\right)_p = 0.242 \left(\frac{181.96}{(333)^2} - \frac{1104.8 \times 0.76}{(333)^3}\right)$$

$$= 0.0003901$$

The sum of these two (of which the first is almost negligible) is 0.0003947. Multiplying by 0.76 we get

$$\left(\frac{\partial c_p}{\partial p}\right)_T = 0.000300 \text{ cal. per gm. per deg. per atm.}$$

The value from Holborn and Jacobs' empirical interpolation formula is

0.000286 cal. per gm. per deg. per atm.

and from their observations at their lowest pressures (namely 1 and 25 atmospheres)

0.000312 cal. per gm. per deg. per atm.

This would be called good corroborative agreement. (Holborn and Jacobs' empirical formula is

$$\left[10^4 c_p = 2413 + 2.86p + 0.0005p^2 - 0.00001 p^3 \right]$$

There is one general comparison here that is of interest, namely the bearing of calorimetric measurements on the characteristic equation through the relation

$$\left(\frac{\partial c_p}{\partial p} \right)_T = - T \left(\frac{\partial^2 v}{\partial T^2} \right)_p$$

already employed, and the direct experiments upon it. Thus the two lines of calorimetric measurements on $\left(\frac{\partial c_p}{\partial p} \right)_T$ above compared are in agreement; whereas the values of the absolute zero obtained from the two sources, namely, the Joule-Thomson effect and the characteristic equation are at some variance. We are at least, then, entitled to a suggestion that perhaps there is some source of constant error in the direct measurements of the characteristic equation, say on the volume as already pointed out due to some surface action. Experiments on volumes differing in a large ratio would test this point.

Summary.

1. Experiments have been carried out on the Joule-Thomson effect for air using the radial-flow form of porous plug, platinum resistance thermometers connected differentially, and a novel form of pressure regulator.

2. The pressure and temperature drops were small, the former lying between 0.25 and 0.80 meters of mercury. The mean pressure of the experiments lay between 4.5 and 6.4 meters of mercury, the mean temperatures between 15° C and 90° C.

3. The Joule-Thomson coefficient, $\mu = \frac{\Delta t}{\Delta p}$, was found to vary with both pressure and temperature, being expressible by either of the two formulae:

$$\mu = + 0.3935 - 0.00691\,p - 0.001835\,t + 0.00000134t^2 + 0.0000325pt$$

or

$$\mu = -0.2599 + 181.96\,\frac{1}{T} - 552.42\,\frac{p}{T^2}\ ;$$

all pressures being expressed in meters of mercury, t in degrees C, and T = 273 + t.

4. Accidental errors in these measurements are reduced to the order of less than one percent

5. Values for the temperature of the ice point on the thermodynamic scale of temperatures were computed, by aid of the two above formulae, resulting in:

273.°36 (three-constant formula)

273.°37 (five-constant formula)

6. Values for the correction to the constant-pressure air thermometer reducing its readings to the thermodynamic scale within the fundamental interval were computed and tabulated (Table IV). Good agreement is found with the values of other writers.

7. Values of the pressure coefficient of c_p are computed and compared with recent work.

Acknowledgments. My thanks are due to Professor Ames, who suggested the work, for his encouragement and continual interest throughout its course; to my associate Professor C. M. Sparrow, for aid in making computations, and for valuable criticisms and suggestions in regard to theory, and to my colleague Professor Mitchell for aid in the least square reductions. In addition I have gained valuable information on experimental matters from the Bureau of Standards, particularly from Messrs. H. C. Dickinson and N. S. Osborne. For mechanical work I am indebted to Messrs. A. W. Barlow, I. J. Shepherd and M. M. Fitzhugh, students, who at various times have done mechanicians work on the apparatus.

Bibliography.

1. Joule, J. P. and Thomson, Wm. On the Thermal Effects of Fluids in Motion.

Collected Papers (Thomson) I, p. 333
or
Scientific Papers (Joule) II, p. 216.

2. Regnault, H. V.

Relation des Expériences III, p. 700.

3. Hirn, G. A.

Théorie Méc. de la Chaleur (3ème ed.), II, p. 387

4. Griessmann.

Zeitsch. ver d. Ing. 47, 1852 and 1880 (1903) also.

Forschungsarb. ver d. Ing. 13, 1, (1904).

5. Grindley.

Phil. Trans. 194 A, 1 (1900-1).

6. Peake

Proc. Roy. Soc. A, 76, 185 (1905).

7. Dodge

Jour. Am. Soc. Mech. Engs. 28, 1265 (1907) and 30, 1227,(1908)

8. Davis, H. N. On the Applicability of the Law of Corresponding States to the Joule-Thomson Effect in Water and Carbon Dioxide.

Proc. Am. Ac. Arts and Sciences 45, 203, (1910).

9. Cazin, A. Le Travail Intérrieur dans les Gaz.

Ann. de Chim. et de Phys. (4), 19, 5, (1870)

10. Natanson, E. Ueber die Abkühlung der Kohlensäure bei ihrer Ausdehnung.

Wied. Ann. 31, 502 (1887).

11. Kester, F. E. The Joule-Thomson Effect in Carbon Dioxide.

I. Experimental.

Phys. Rev. 21, 260, (1905).

12. Olszewski, K. Bestimmung der Inversionstemperatur der Kelvinschen Erscheinung für Wasserstoff.

Ann. d. Phys. (4), 7, 818, (1902)

13. Olszewski, K. Temperature of Inversion of the Joule-Kelvin Effect for Air and Nitrogen. Preliminary Communication.

Phil. Mag. (6), 13, 722, (1907).

14. Rudge, W. A. D. A Constant Temperature Porous Plug Experiment.

Phil. Mag. (6), 18, 159, (1909).

15. Bradley, W. P. and Hale, C. F. The Nozzle Expansion of Air at High Pressure.

Phys. Rev. 29, 258, (1909).

16. Dalton, J. P. Researches on the Joule-Kelvin effect especially at low temperatures. I. Calculations for hydrogen. II. The Joule-Kelvin effect for air at 0°C. and at pressures up to 42 atmospheres.

Comm. Phys. Lab. Leiden. 109a and 109 c (1909).

17. Vogel, E.

Dissertation, München 1910 and

Z. S. f. Kompr. u. fl. Gase 14, 3, 25, 117, 131, 159, 175 (1910-11)

18. Noell, F. Ueber die Temperaturänderung von Luft ohne äussere Arbeitsleistung by Drucken bis zu 150 Atmosphären und Temperaturen von + 250 bis - 55°C.

Sitzungsberichte, München M. u. Ph. Kl. 213 (1912)

and

Die Abhängigkeit des Thomson-Joule Effektes für Luft von Druck und Temperature by Drucken bis 150 At. und Temperaturen von -55°C bis + 250°C.

Ann. Beibl. 39, 777 (1915)

Dissertation, München (1914).

19. Witkowski, A. W. Über die Abkühlung der Luft durch nicht unkehrbare Druckverminderung.

Bull. Acad. Sc. Krakau 282 (1898).

20. Roebuck, J. R. A. Porous Plug Method for the Mechanical Equivalent of Heat.

Phys. Rev. 2, 79, (1913).

21. Lehfeldt, R. A. A Numerical Evaluation of the Absolute Scale of Temperature.

Phil. Mag. 45, 363, (1898).

22. Callendar, H. L. On the Thermodynamical Corrections of the Gas-Thermometer.

Phil. Mag. (6) 5, 48, (1903).

23. Rose-Innes, J. On the Practical Attainment of the Thermodynamic Scale of Temperature.

Phil. Mag. (6) 2, 130, (1901)
" " " 6, 353, (1903)
" " " 15, 301, (1908).

24. Buckingham, E. On the Establishment of the Thermodynamic Scale of Temperature by means of the Constant Pressure Thermometer.

Bull. Bureau of Stand. 3, 237, (1907).
and
The Thermodynamic corrections of the Nitrogen Scale.

Phil. Mag. (6), 15, 526 (1908).

25. Berthelot, D. Sur les Thermomètres à Gaz et sur la Reduction de leurs Indications à l'Echelle absolue des Temperatures.

Trav. et Mém. Bur. Int. 13, (1903)

also " " " 13, (1907).

26. Derwin, H.

An Electric Thermostat.

Astrophys. Jl. 20, 347, (1904).

27. Randall, H. M. Expansion of Fused Quartz at High Temperatures.

Phys. Rev. 30, 221, (1910).

28. Carey Foster, G.

Phil. Mag. May, 1884.

29. Callendar, H. L. Platinum Thermometry.

Phil. Mag. 47, 191, (1899).

30. Burnett and Roebuck. On a Radial Flow Porous Plug and Calorimeter.

Phys. Rev. 30, 529, (1910).

31. Buckingham, E. On a Modification of the Plug Experiment.

Phil. Mag. (6), 6, 518, (1903).

33. Swann, W. F. G.

On the Specific Heats of Air and Carbon Dioxide at Atmospheric Pressure by the Continuous Electric Method at 20° C and 100° C.

Phil. Trans. (A) 210, 199, (1910).

32. Chappius, P.

Nouvelles Études sur les Thermomètres á Gaz.

Trav. et Mém du Bureau Int. des Poids et Mésures 13, (1907).

34. Holborn and Jacob. C_p for air at 60° and 1-200 atmospheres.

Sci. Abstr. No. 866 (1915).

Zeit. Vereines Deutsch. Ing. 58, 1429 (1914).

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Life.

Llewellyn Griffith Hoxton was born April 28, 1878 at the Episcopal High School near Alexandria, Va., where he received his early education. From 1896 to 1900 he studied at the University of Virginia taking the degrees of B.A., B.S. and M.A. in 1900.

From 1901 to 1905 he held the posts of Laboratory Assistant and Assistant Physicist in the Bureau of Standards, Washington, D.C. Part of the same time he took graduate lectures at the Johns Hopkins University, studying under Professors Ames, Wood, Whitehead, Cohen and Reid. In the summer of 1905 he accepted the position of Assistant on Great Equatorial in the U. S. Naval Observatory Eclipse Expedition to Spain and Africa.

He was Fellow in Physics at the Johns Hopkins University in 1905-6 and since that time has been Adjunct and then Associate Professor of Physics at the University of Virginia.

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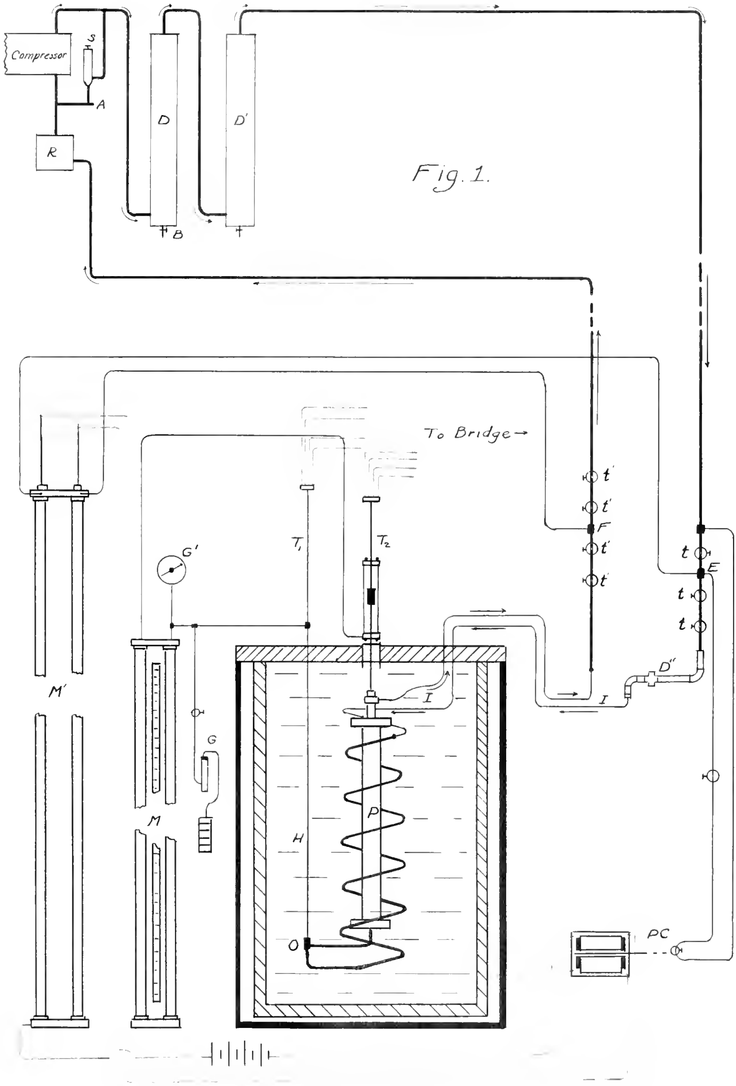


Fig. 1.

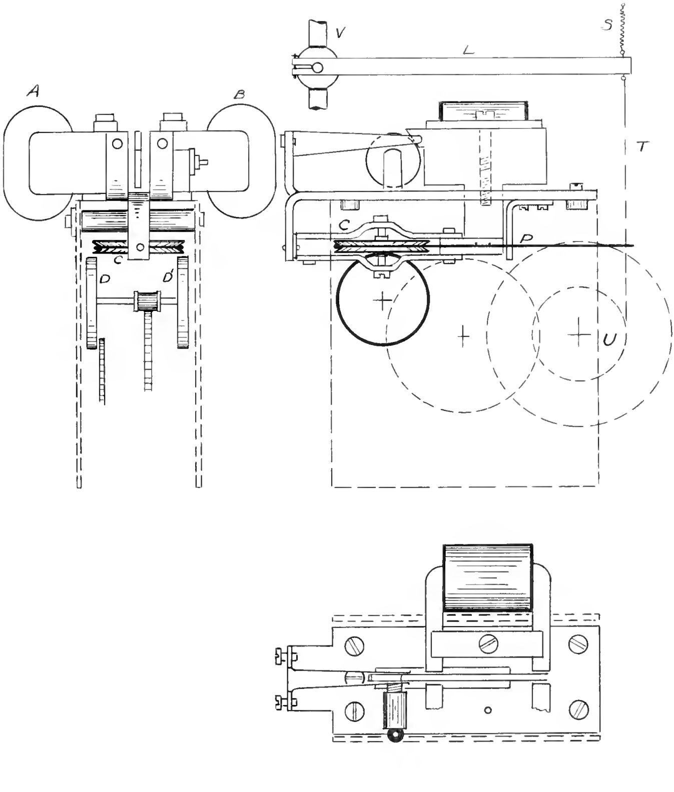


Fig. 2.

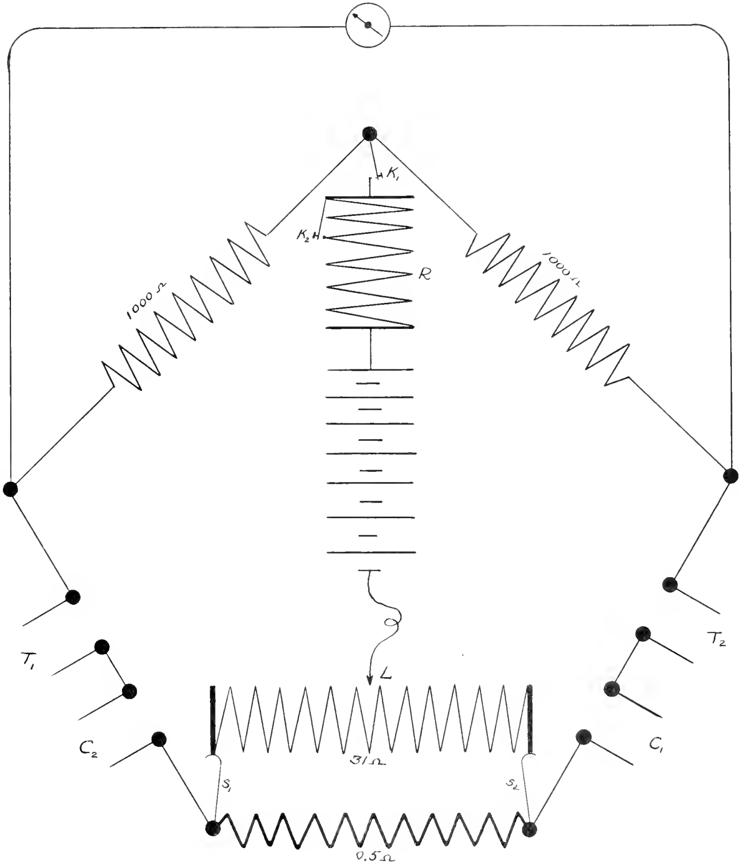


Fig. 3.

FOLD OUT

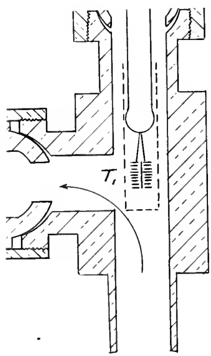


Fig.

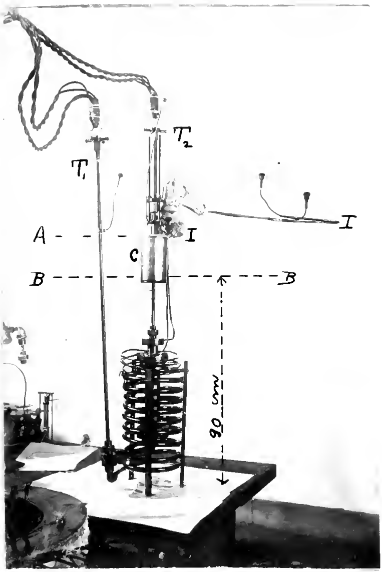


Fig. 5.

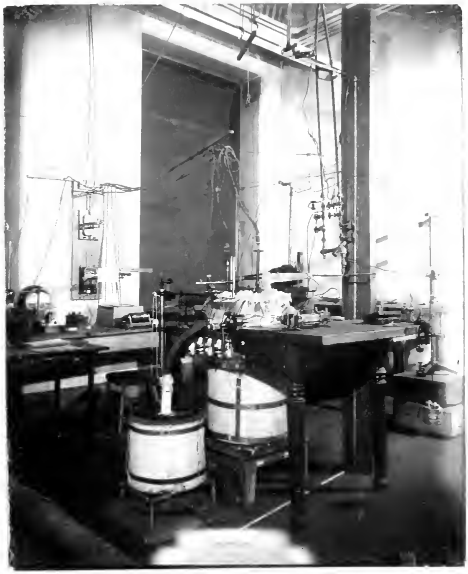
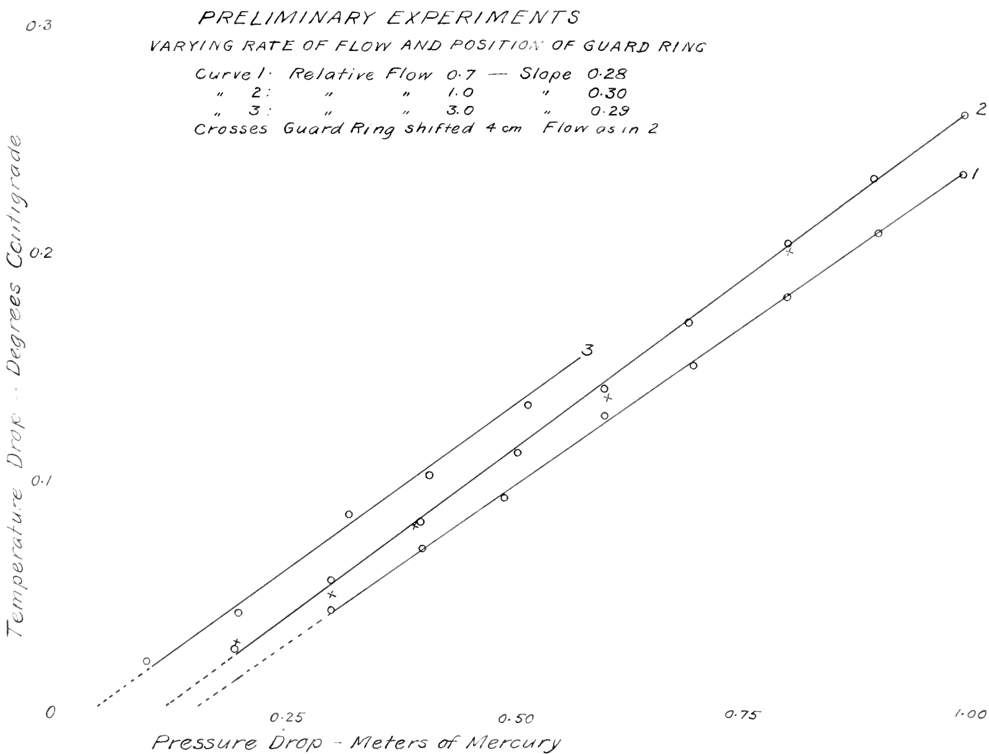


Fig 6.


PRELIMINARY EXPERIMENTS
VARYING RATE OF FLOW AND POSITION OF GUARD RING
Curve 1: Relative Flow 0.7 — Slope 0.28
" 2: " " 1.0 " 0.30
" 3: " " 3.0 " 0.29
Crosses Guard Ring shifted 4 cm Flow as in 2
1
2
3
0
0.1
0.2
0.3
0.25
0.50
0.75
1.00
Temperature Drop - Degrees Centigrade
Pressure Drop - Meters of Mercury

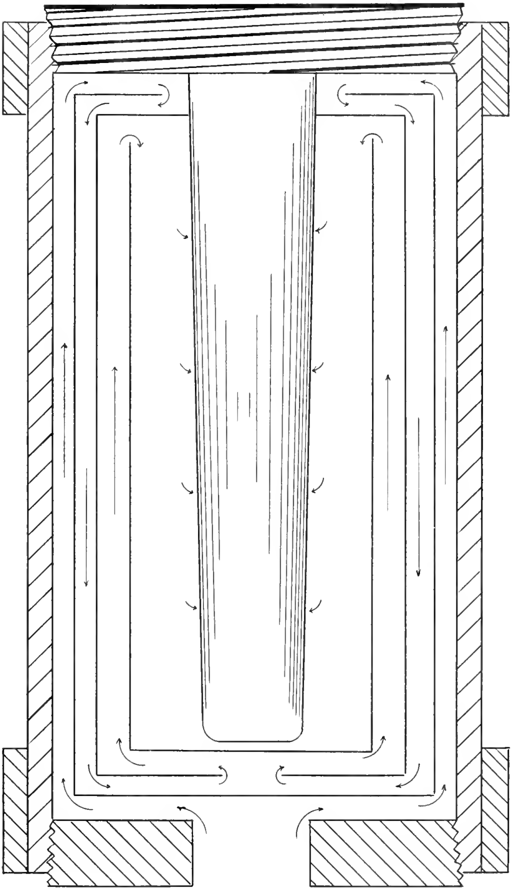
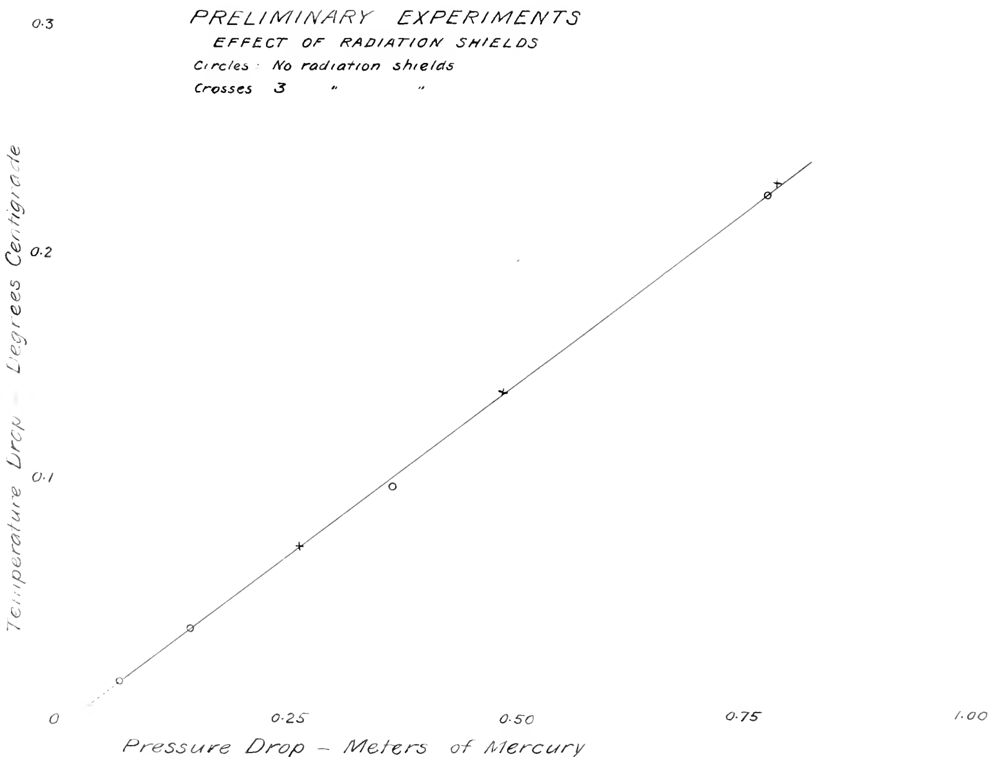
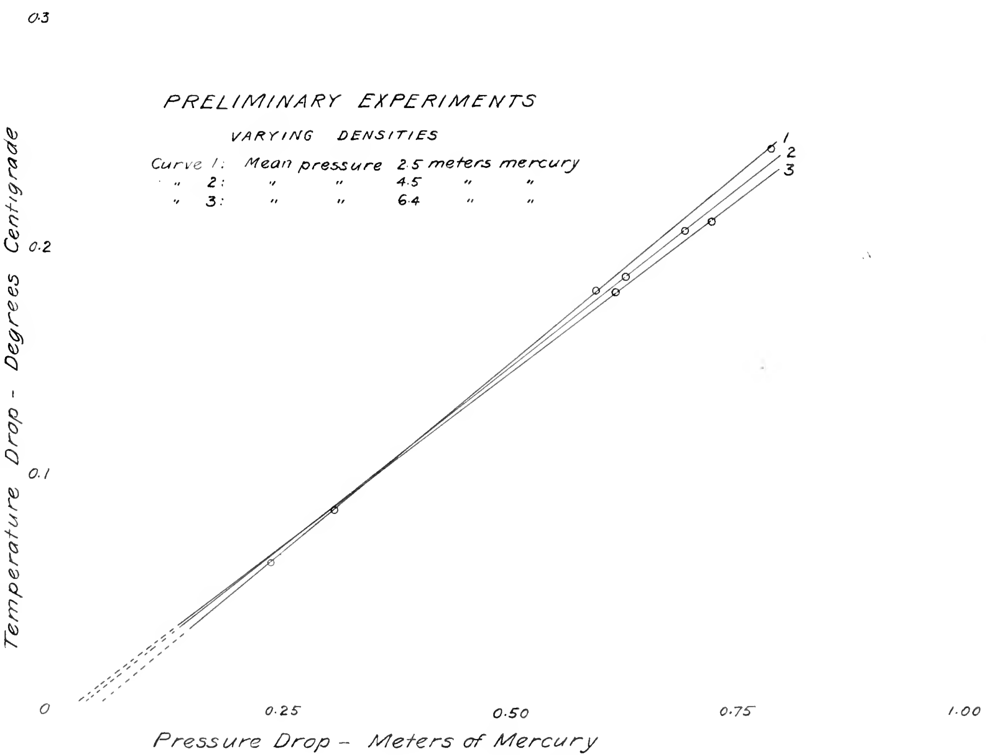


Fig. 8.



PRELIMINARY EXPERIMENTS
EFFECT OF RADIATION SHIELDS
Circles: No radiation shields
Crosses 3 " "
0.3
0.2
0.1
0
0.25
0.50
0.75
1.00
Temperature Drop - Degrees Centigrade
Pressure Drop - Meters of Mercury



PRELIMINARY EXPERIMENTS
VARYING DENSITIES
Curve 1: Mean pressure 2.5 meters mercury
" 2: " " 4.5 " "
" 3: " " 6.4 " "
1
2
3
0.3
0.2
0.1
0
0.25
0.50
0.75
1.00
Temperature Drop - Degrees Centigrade
Pressure Drop - Meters of Mercury

Fig 10

JOULE-THOMSON COEFFICIENT

AS A FUNCTION OF TEMPERATURE AND PRESSURE

Curves are graphs of the formula

$$\mu = -0.2599 + 181.96\frac{1}{T} - 552.42\frac{p}{T^2}$$

Circles are observed values